

SYSTEM UNIT FOR DESORBING CARBON DIOXIDE FROM METHANOL

The object of the invention is a system unit, which in the total purification of compressed gases, makes it possible to recover methanol in a pure state and at the same time utilize the cold energy liberated in an extremely effective way.

It is known that cold methanol has the capability of absorbing large amounts of gas impurities. Use is made of this capability in the Rectisol[®] process, in which the total purification of compressed gases is possible in a single process operation. The absorptive capability of methanol increases considerably at lower temperatures. At -60 °C for example 75 times more carbon dioxide dissolves in methanol than in the same volume of water at 25 °C, that is the methanol cycle amounts to 1/75 compared with water recirculation in a pressurized water cycle. At lower temperature the vapor pressure of methanol is so low that there is little use of solvent.

The Rectisol[®] process is particularly efficient when large amounts of gas impurities must be removed, or if a particularly high gas purity is required, and overall where the process can be built into the cold stage of a low temperature gas decomposition. In the latter case the process itself offers important advantages when only small quantities of gaseous impurities are to be washed out.

Gas washing is carried out such that the standing raw gas is treated with methanol under medium pressure of 5 to 40 atmospheres or also under high pressure of 50 to 200 atmospheres at temperatures between 10 °C and -80 °C.

Thereby, all gaseous impurities such as raw gasoline, crude benzene, ammonia, hydrocyanic acid, resin formers, organic sulfur and phosphorus compounds, carbonic acid, hydrogen

sulfide, iron and other metal carbonyls and water are absorbed. The loaded up methanol is then regenerated by expansion, evaporation, or heating, and subsequently re-used. The impurities can be recovered from the off-gases or condensate. This process is the subject of German patent 1 544 080.

An especially important gas purification process known to the art includes purification of, for example, synthesis gases, produced from natural gas gasification processes, which are the starting point for a variety of major technical syntheses. Raw synthesis gas contains considerable amounts of carbon dioxide the removal of which is crucially important for the further use of synthesis gasses. The development of effective, reliable, and cost effective processes for removal of carbon dioxide from synthesis gasses is therefore of considerable importance for the efficient winning of a variety of applicable gas mixtures.

It has now been found that the process known up until now for the purification of gases with methanol may still be improved considerably, if the system unit in accordance with the invention, and the process that may be carried out therein for desorption of carbon dioxide, is employed.

The object of the invention is therefore a system unit for desorption of carbon dioxide and other impurities from methanol held under high pressure, comprising one or a plurality of expansion vessels arranged in sequence, at least one heat exchanger and at least one liquid/gas separator, in which

- (a) A line (1) is provided through which the strongly cooled methanol leaving the expansion vessel C is introduced from below into the heat exchanger and

- (b) a line (2) is provided, through which the heated methanol above is transported from the top of the heat exchanger E, and is connected to a liquid/gas separator, in which the remaining carbon dioxide contained in the methanol is desorbed and separated to the greatest extent possible.

Figure 1 shows an entire installation for desorption of carbon dioxide and other impurities from methanol held at high pressure, while figure 2 depicts the system unit in accordance with the invention and discloses further technical details thereby.

For effective implementation of the process in accordance with the invention it is of great importance that the three reaction vessels C, D and E be arranged at a carefully determined height relative to each other. That allows one in fact to ensure that the liquid flows in the wanted direction through the heat exchanger E, without a pump being necessary. Liquid flow known as the thermo-siphon effect develops automatically as a result of gravity and the condensing carbon dioxide. That can only be achieved though in the system unit in accordance with the invention

- (a) the liquid level in the expansion vessel C is located about 1 to 20 m above the liquid level in the liquid-gas separator;
- (b) this again is located about 0.5 m above the top of discharge opening for the heated methanol provided in the heat exchanger E;
- (c) the distance between the inlet line (1), from the bottom of the heat exchanger E, for the methanol fed from the expansion vessel C, and the base of the heat exchanger E is about 0.5 m.

Self-evidently the system unit in accordance with the invention can be operated by use of pumps, however it is particularly advantageous to exploit application of the thermo-siphon effect so to automatically establish liquid flow through the various components of the system unit in accordance with the invention.

The system unit in accordance with the invention is downstream to an absorber (5), which is provided for purification of synthesis gas with methanol. In addition, in accordance with the invention a regenerator (6) is downstream to the system unit, in which, by further increasing the temperature and influx of a heated inert gas - such as for example methanol vapor - the remaining carbon dioxide is desorbed from the methanol,.

In the absorber (5) the raw gas flowing in from below through the counter-flowing cold methanol, is purified. The outgoing liquid from below the absorber (5), containing all impurities of the raw gas, is cooled in the heat exchanger E and fed into the expansion vessel (A). The purified synthesis gas leaves at the top of the absorber.

In the expansion vessel A the methanol held under a pressure of 55 atmospheres is expanded to about 9 atmospheres and at a temperature of -45°C desorbs mainly hydrogen and carbon monoxide, which after passage through the heat exchanger E are obtained as gas fraction for the process. The liquid fraction from the expansion vessel A is then fed through a line to a second expansion vessel B.

In expansion vessel B the methanol pressure is lowered from about 9 atmospheres to about 2.7 atmospheres and thereby a temperature decrease from about -45°C to about -52°C is obtained. In this case gaseous carbon dioxide is released from the methanol, which is passed through the heat exchanger E and may subsequently be credited to the process,

while the liquid fraction obtained is fed to a third expansion vessel C.

In expansion vessel C the pressure of the methanol solution is decreased from about 2.7 atmospheres to about 1.2 atmospheres and thereby a further temperature decrease from about -52 °C to about -60 °C is observed. Also in this expansion vessel, gaseous carbon dioxide is obtained, which likewise is fed to heat exchanger E and can subsequently be credited to the process.

The liquid fraction obtained in expansion vessel C is then preferably divided into two streams, wherein one stream is fed to the upstream absorber (5) and the second stream is fed through line 1 to the heat exchanger E, which in its case, for the methanol heated there, is connected by line (2) with the liquid-gas separator D.

The liquid-gas separator D has a branch line (3) for gaseous carbon dioxide, as well as another line in which the liquid methanol is taken from below the separator and fed to the downstream regenerator (6). The liquid fraction (4) taken from the liquid/gas separator is fed to the downstream regenerator (6) to remove the last traces of carbon dioxide, which are extracted by further increasing the temperature and feeding in a stream of heated gas, for example methanol vapor. While the carbon dioxide is taken from the process, the ultrapure methanol produced in the regenerator is fed back to the absorber (5) and remains there to be available again for the purification of a fresh stream of raw gas.

Overall the process in accordance with the invention is therefore characterized in that carbon dioxide is desorbed from methanol stepwise in a plurality of expansion vessels, at least one heat exchanger, and at least one liquid/gas separator. Here the methanol leaving the expansion vessel

has a temperature of -60 ± 10 °C and a pressure of 1 to 2 atmospheres. The cold liberated by the heat exchanger E represents a valuable energy source available for other cooling reactions.---In this instance the temperature of the methanol stream increases in the heat exchanger to -10 ± 5 °C, and the liquid stream is fed to the liquid/gas separator at this temperature.

The process in accordance with the invention and the system unit associated with it thus make possible in an exceptionally purposeful manner the purification of enriched methanol, in the total removal of the contained pressurized gases and impurities, especially carbon dioxide. At the same time, the cold of vaporization resulting from desorption of carbon dioxide is recovered which is of great significance for absorption processing.

The material streams in the system unit in accordance with the invention show the indicated parameters in table 1 below.

Material Stream	1	2	3	4
Stream Parameters				
Carbon Dioxide	11.45	11.45	98.10	1.44
Methanol	88.55	88.55	1.92	98.56
Temperature	-59.5	-8.8	-8.9	-8.9
Pressure (in absolute atmospheres)	1.20	1.20	1.15	1.15
Vapor Proportion	0.00	0.10	1.00	0.00
Flow Velocity (t/h)	585	585	80	505